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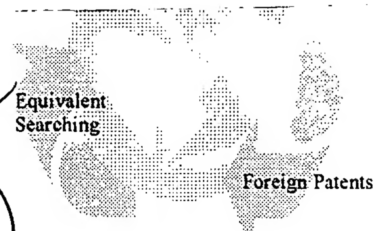

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COPPER ALLOY FOR WELDED TUBE
[Yosetsukan yo dougohkin]

Susumu Kawauchi et al.

UNITED STATES PATENT AND TRADEMARK OFFICE
Washington, D.C. June 2001

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FOREIGN TITLE	[54A]:	YOSETSUKAN YO DOUGOHKIN

Specification

1. Title of the Invention

Copper alloy for welded tube

2. Claims

(1) Copper alloy for a welded tube consisting of 25 to 40 wt% of zinc, 0.005 to 0.070 wt% of phosphorus, 0.05 to 2.0 wt% of nickel, and 0.05 to 1.0 wt% of tin, the balance consisting of copper and inevitable impurities.

(2) Copper alloy for a welded tube consisting of 25 to 40 wt% of zinc, 0.005 to 0.070 wt% of phosphorus, 0.05 to 2.0 wt% of nickel, and 0.05 to 1.0 wt% of tin, the balance consisting of copper and inevitable impurities, in which the crystal particle size is adjusted to 0.015 mm or smaller in the final annealing operation.

3. Detailed Explanation of the Invention

This invention relates to copper alloy for a welded tube having excellent corrosion resistance and weld cracking proofness at the welded part.

In recent years, in thin copper alloy tubes, welded tubes which are formed by high-frequency resistance welding or high-frequency induction welding have been used. This trend is especially remarkable in tubes used in radiators. Conventionally, lock seam tubes are used in radiators. However, because of the requirements for a cost reduction and a production efficiency increase, welded tubes formed by high-frequency

resistance welding or high-frequency induction welding are being used. However, copper alloy welded tubes have a shortfall such that corrosion resistance of the welded part is significantly inferior compared to other parts because of the unusualness of its welded structure. Considering the worsening environmental conditions within which the tubes have been used in recent years, such a shortfall can significantly limit the usage of such copper alloy welded tubes. Furthermore, when a high-frequency induction welding technique or a high-frequency resistance welding technique is used in the manufacture of copper alloy welded tubes, weld cracking can easily occur. Under such a situation, materials having excellent corrosion resistance at the welded part and low susceptibility to weld cracking are in demand.

As a result of research conducted under such a situation, there were developed copper alloy for a welded tube, in which corrosion resistance is improved, consisting of 25 to 40 wt% of zinc, 0.005 to 0.070 wt% of phosphorus, 0.05 to 2.0 wt% of nickel, and 0.05 to 1.0 wt% of tin, the balance consisting of copper and inevitable impurities; and copper alloy for a welded tube, in which corrosion resistance is improved and weld cracking proofness is improved, consisting of 25 to 40 wt% of zinc, 0.005 to 0.070 wt% of phosphorus, 0.05 to 2.0 wt% of nickel, and 0.05 to 1.0 wt% of tin, the balance consisting of copper and inevitable impurities, in which the crystal particle size is adjusted to 0.015 mm or smaller in the final annealing operation.

Regarding the alloy constituent in copper alloy for a welded tube, its action and the reasons for its limitation to an addition quantity, and the crystal particle size are explained. Copper and zinc are basic

constituents of the invented alloy. They are excellent in processability, mechanical strength, and thermal conductivity. If the zinc content is less than 25 wt%, the processability is worsened. If the zinc content exceeds 40 wt%, a deposit of β-phase appears in the copper-zinc alloy, and corrosion resistance and cold rolling processability are worsened. If the phosphorus content is less than 0.005 wt%, no improvement is made in its corrosion resistance. If the phosphorus content exceeds 0.070 wt%, although the corrosion resistance can be improved, signs of grain boundary corrosion are observed. If the nickel content is less than 0.05 wt%, there is no improvement in corrosion resistance of the welded part. If the nickel content exceeds 2.0 wt%, the effect of corrosion resistance improvement saturates. If the tin content is less than 0.05 wt%, there is no improvement in corrosion resistance of the welded part. If the nickel content exceeds 1.0 wt%, the effect of corrosion resistance improvement saturates. As explained above, corrosion resistance of the raw material is improved by the addition of phosphorus, and corrosion resistances of the raw material and the welded part are improved by the addition of nickel and tin. The reason for limiting the crystal particle size to 0.015 mm or lower is explained next. As a result of investigating the reason for weld cracking caused by high-frequency induction welding or high-frequency resistance welding, the inventors found that if the grain boundary is in contact with the molten base metal material, the grain boundary is embrittled, and when a slight impact is received, weld cracking occurs. As a result of investigating such a phenomenon, it was observed that the effect of the crystal particle size is large, and by making the crystal

particle size small, susceptibility to such a phenomenon can be significantly reduced.

The crystal particle size is limited to 0.015 mm or smaller, because if the crystal particle size exceeds 0.015 mm, weld cracking easily occurs.

Working Examples

Alloys having the composition shown in Table 1 were melted, and were subjected to hot rolling and cold rolling with proper annealing to form 1 mm thick plates. Ultimately, they were subjected to annealing at various temperatures to adjust the crystal particle size to those shown in Table 1. These plates thus prepared were used in testing. Welding materials to be used in corrosion resistance test were manufactured by a butt TIG welding of 1 mm thick alloys whose composition is shown in Table 1. For the corrosion resistance test, a solution in which

sodium bicarbonate	1.3 g/l
sodium sulfate	1.5 g/l
sodium chloride	1.6 g/l

were dissolved in 1 l of distilled water was held at a liquid temperature of 88°C, and air was introduced at a rate of 100 ml/minute. Test samples were immersed in this solution for 240 hours. The maximum dezincing corrosion depth generated at this time at the welded part was measured. With this measured value, the corrosion resistance was evaluated. Results are shown in Table 2.

A test for resistance to the occurrence of weld cracking by the embrittlement of the grain boundary when in contact with the molten base metal material is performed by the following method. 1 mm thick alloys

having the composition shown in Table 1 were processed to a pipe shape as shown in Figure 1. This alloy pipe was then immersed in the molten metal of the same composition which was held at the melting point +50°C for 3 seconds. Thereafter, it was removed from the molten metal, and in the state at which the adhered metal was melted in the holding furnace, an impact was imposed as shown in Figure 2. The cross-sectional surface of the deformed pipe was observed with a microscope to confirm whether there was an intergranular fracture. Resistance to weld cracking was evaluated using this observed result. Results are shown in Table 3.

From Table 2 and Table 3, it is known that the invented alloys have excellent corrosion resistance toward the dezincing corrosion of the welded part and weld cracking proofness can be improved.

In other words, in the comparison alloys (Tests No. 1 to 5), the maximum dezincing corrosion depth was 347 μ to 603 μ at the welded part, while in the invented alloys (Tests No. 6 to 20), the maximum dezincing corrosion depth was 48 μ to 104 μ at the welded part. It is known from these results that the invented alloys have far superior dezincing corrosion resistance.

Furthermore, with the invented alloys in which the crystal particle size is 0.015 mm or smaller (Tests No. 7 to 11, 14, 18 to 20), there is only ductile deformation but no occurrence of cracking according to the weld cracking test method shown in Figure 2, indicating improvement in weld cracking proofness. In contrast, an intergranular fracture occurs in those in which the crystal particle size exceeds 0.015 mm. Thus, they are undesirable.

Therefore, the crystal particle size is adjusted depending on the

usage of the tubes.

As described above, the invented alloys have excellent characteristics as copper alloy for a welded tube.

TABLE 1

(unit: wt%)

	Zn	P	Ni	Sn	Cu	Crystal particle size (mm)
Comparison alloy 1	30	–	–	–	balance	0.080
" 2	35	–	–	–	"	0.030
" 3	28	0.002	0.01	0.01	"	0.025
" 4	37	0.001	0.03	0.02	"	0.050
" 5	33	0.002	0.02	0.01	"	0.040
Invented alloy 6	26	0.01	0.1	0.1	"	0.030
" 7	30	0.06	1.0	0.3	"	0.015
" 8	35	0.04	0.3	0.2	"	0.005
" 9	33	0.02	0.08	0.07	"	0.010
" 10	30	0.03	0.8	0.6	"	0.010
" 11	38	0.05	1.3	0.9	"	0.005
" 12	27	0.01	0.4	0.2	"	0.025
" 13	32	0.02	1.8	0.5	"	0.050
" 14	35	0.05	0.5	0.2	"	0.005
" 15	30	0.03	0.1	0.8	"	0.030
" 16	36	0.008	0.6	0.1	"	0.020
" 17	33	0.04	1.1	0.06	"	0.050
" 18	28	0.02	0.08	0.3	"	0.010
" 19	31	0.03	1.5	0.9	"	0.015
" 20	35	0.01	0.7	0.2	"	0.005

TABLE 2

	Maximum dezincing corrosion depth (μ)
	Welded part
Comparison alloy 1	567
" 2	603
" 3	347
" 4	391
" 5	683
Invented alloy 6	104
" 7	74
" 8	90
" 9	103
" 10	99
" 11	48
" 12	92
" 13	49
" 14	72
" 15	68
" 16	99
" 17	65
" 18	100
" 19	55
" 20	83

TABLE 3

	Deformation state
Comparison alloy 1	intergranular fracture
" 2	"
" 3	"
" 4	"
" 5	"
Invented alloy 6	"
" 7	ductile deformation
" 8	"
" 9	"
" 10	"
" 11	"
" 12	intergranular fracture
" 13	"
" 14	ductile deformation
" 15	intergranular fracture
" 16	"
" 17	"
" 18	ductile deformation
" 19	"
" 20	"

4. Brief Explanation of Drawings

Figure 1 is a 1 mm thick alloy pipe cross-sectional diagram to be used in a weld cracking proofness test. Figure 2 is an explanatory diagram showing a weld cracking proofness test device.

1: 1 mm thick alloy pipe (length: 10 mm)

2: free falling body (weight: 200 gw)

3: supporting state

4: heating holding furnace

a: pipe inside diameter (ϕ 20 mm)

b: pipe outside diameter (ϕ 22 mm)

c: falling distance of the falling body (2) (50 mm)

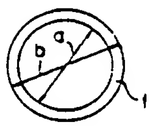

Figure 1

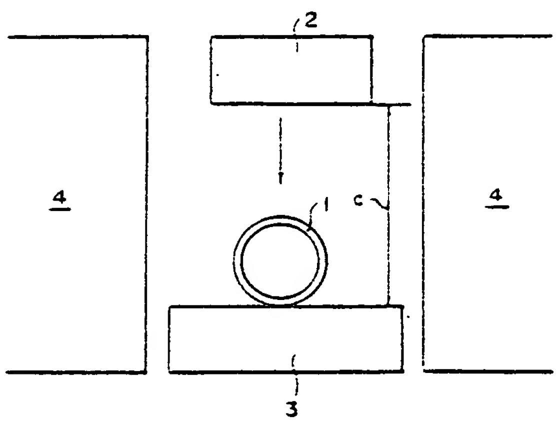

Figure 2

⑲ 日本国特許庁（JP）　⑪ 特許出願公開

⑫ 公開特許公報（A）　昭59—126742

⑤Int. Cl.³ C 22 C 9/04　識別記号 CBG　庁内整理番号 6411—4K　㊸公開 昭和59年(1984) 7月21日

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⑭溶接管用銅合金

㉑特　願　昭58—474
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明　細　書

1. 発明の名称

溶接管用銅合金

2. 特許請求の範囲

(1) 亜鉛25～40wt%，りん0.005～0.070wt%，ニッケル0.05～2.0wt%，錫0.05～1.0wt%を含み，残部銅及び不可避的な不純物からなる溶接管用銅合金。

(2) 最終焼鈍で結晶粒度が0.015mm以下となるように調整された亜鉛25～40wt%，りん0.005～0.070wt%，ニッケル0.05～2.0wt%，錫0.05～1.0wt%を含み，残部銅及び不可避的な不純物からなる溶接管用銅合金。

3. 発明の詳細な説明

本発明は優れた溶接部の耐食性，耐溶接割れ性を有する溶接管用銅合金に関するものである。

近年薄肉の銅合金管は高周波抵抗溶接もしくは高周波誘導溶接による溶接管が用いられるようになつてきた。この傾向は特にラジエーターに使用されるチューブについて顕著である。従来ラジエーターにはロックシームチューブが使用されてきたが，コスト低減と生産効率の上昇の要求から高周波抵抗溶接もしくは高周波誘導溶接による溶接チューブが採用されるようになりつつある。しかしながら銅合金溶接管はその溶接組織の特異性からその溶接部は他の部分と比較して耐食性が大幅に劣るという欠点を持つている。このことは近年の使用環境の悪化等から考えると銅合金溶接管の使用上の大きな制約となる。さらには銅合金溶接管の製造の際に溶接方法として高周波誘導溶接もしくは高周波抵抗溶接を用いた場合，溶接割れを発生しやすいという製造上の難点を持つている。このような状況から溶接部の耐食性が優れ，かつ溶接割れ感受性の低い材料が要求されている。

本発明はこのような状況を鑑みて研究を行なつた結果，亜鉛25～40wt%，りん0.005～0.070wt%，ニッケル0.05～2.0wt%，

WEST

錫0.05～1.0wt%を含み，残部銅及び不可避的な不純物よりなる耐食性を向上させた溶接管用銅合金及び亜鉛25～40wt%，りん0.005～0.070wt%，ニッケル0.05～2.0wt%，錫0.05～1.0wt%を含み，残部銅及び不可避的な不純物よりなる最終焼鈍で結晶粒度が0.015mm以下となるように調整された耐食性を向上させ，かつ耐溶接割れ性の向上した溶接管用銅合金を開発した。

本発明の溶接管用銅合金における合金成分についてその作用と添加量及び結晶粒度の限定理由について説明する。銅と亜鉛は本発明合金の基本成分となるもので，加工性，機械的強度に優れていると共に，熱伝導性にも優れている。亜鉛添加量を上記範囲に限定した理由は，亜鉛が25wt%未満では加工性が悪くなることと及び亜鉛が40wt%を越えると銅－亜鉛合金におけるβ相の析出がみられ耐食性及び冷間加工性が悪くなるためである。りんの添加量を0.005～0.070wt%とする理由は，りんの添加量が0.005wt%未満では耐食性の向上がみられず，また0.070wt%を越えると耐食性は向上するが，粒界腐食の徴候がみられるためである。ニッケルの添加量を0.05～2.0wt%とする理由は，ニッケルの添加量が0.05wt%未満では溶接した場合溶接部の耐食性の向上がみられず，また2.0wt%を越えると耐食性向上の効果が飽和するためである。錫の添加量を0.05～1.0wt%とする理由は，錫の添加量を0.05wt%未満では溶接した場合の溶接部の耐食性の向上がみられず，また1.0wt%を越えると耐食性向上の効果が飽和するためである。以上のようにりんの添加によつて素材に耐食性を付加し，ニッケルと錫を添加することによつて素材と溶接した場合に溶接部に耐食性を付加するものである。さらに結晶粒度を0.015mm以下に限定した理由について述べる。高周波誘導溶接もしくは高周波抵抗溶接によつて起こる溶接割れの原因について調査した結果，本発明者らは溶融した母材金属と接触していると粒界が脆化して軽い衝撃を受けた場合，溶接割れが発生することを知見した。そこでこのような現象について種々の調査を行なつた結果，結晶粒度の影響が大きく結晶粒度を小さくすることによりこのような現象に対する感受性が大幅に低下することが認められた。

結晶粒度を0.015mm以下に限定した理由は，結晶粒度が0.015mmを越えると溶接割れが発生し易くなるためである。

実施例

第1表に示す諸組成の合金を溶製し熱間圧延及び適宜焼きなましを加えながら冷間圧延により1mm厚さの板とし，最終的に種々の温度で焼きなましを加えて第1表に示される結晶粒度に調整して試験に供した。耐食性試験に供する溶接部材は第1表に示す諸組成の1mm厚さの合金を突き合せTIG溶接することによつて製造した。耐食性試験は1ℓの蒸留水に

炭酸水素ナトリウム　1.3g/ℓ
硫酸ナトリウム　1.5g/ℓ
塩化ナトリウム　1.6g/ℓ

を各々溶かした液を液温88℃に保持し，毎分100mlの空気を吹き込み，この液中に240時間浸漬した。その時発生した最大脱亜鉛腐食深さを溶接部について測定し，これをもつて耐食性を評価した。その結果を第2表に示した。

溶融した母材金属と接触した場合に粒界が脆化して溶接割れの発生に対する耐性についての試験は第1表に示す諸組成の1mm厚さの合金を第1図に示されるようにパイプ状に加工し，これを同一組成の融点+50℃に保持された溶融金属に3秒間浸漬し，その後取り出して保持炉中で付着している金属が溶融している状態で第2図に示されるように衝撃を加えた。その時変形したパイプの断面を顕微鏡によつて観察し粒界破壊の有無を確認し，これをもつて溶接割れに対する耐性を評価した。その結果を第3表に示した。

第2表，第3表からわかるように本発明合金は溶接部の脱亜鉛腐食に対して優れた耐食性を有し，かつ耐溶接割れ性が改善されることが判

明した。

すなわち，比較合金（試料番号1～5）では溶接部の最大脱亜鉛腐食深さが347μ～603μであるのに対し，本発明合金（試料番号6～20）では最大脱亜鉛腐食深さが溶接部48μ～104μであり，本発明合金の耐脱亜鉛腐食性は著しく優れていることが分る。

また本発明合金は，上記のように耐脱亜鉛腐食性に優れているが，さらに結晶粒度が0.015㎜以下であるもの（試料番号7～11, 14, 18～20）は第2図に示す溶接割れ性のテストにおいて単に延性変形するのみで割れの発生がなく，耐溶接割れ性が改善される。逆に結晶粒度が0.015㎜を越えるものについては粒界破壊を起こすので好ましくない。

したがつて結晶粒度の調整は管の用途に応じて適宜実施する。

以上本発明合金は溶接管用銅合金として極めて優れた特性を有するものである。

第 1 表

（単位 wt%）

	亜鉛	りん	ニツケル	錫	銅	結晶粒度（㎜）
比較合金 1	30	—	—	—	残	0.080
〃 2	35	—	—	—	〃	0.030
〃 3	28	0.002	0.01	0.01	〃	0.025
〃 4	37	0.001	0.05	0.02	〃	0.050
〃 5	33	0.002	0.02	0.01	〃	0.040
本発明合金 6	26	0.01	0.1	0.1	〃	0.030
〃 7	30	0.06	1.0	0.3	〃	0.015
〃 8	35	0.04	0.3	0.2	〃	0.005
〃 9	33	0.02	0.06	0.07	〃	0.010
〃 10	30	0.03	0.8	0.6	〃	0.010
〃 11	38	0.05	1.3	0.9	〃	0.005
〃 12	27	0.01	0.4	0.2	〃	0.025
〃 13	32	0.02	1.8	0.5	〃	0.050
〃 14	35	0.05	0.5	0.2	〃	0.005
〃 15	30	0.03	0.1	0.8	〃	0.030
〃 16	36	0.008	0.6	0.1	〃	0.020
〃 17	33	0.04	1.1	0.06	〃	0.050
〃 18	28	0.02	0.08	0.3	〃	0.010
〃 19	31	0.03	1.5	0.9	〃	0.015
〃 20	35	0.01	0.7	0.2	〃	0.005

第 2 表

	最大脱亜鉛腐食深さ（μ） 溶接部
比較合金 1	567
〃 2	603
〃 3	347
〃 4	391
〃 5	483
本発明合金 6	104
〃 7	74
〃 8	90
〃 9	103
〃 10	63
〃 11	48
〃 12	92
〃 13	49
〃 14	72
〃 15	68
〃 16	99
〃 17	65
〃 18	100
〃 19	55
〃 20	83

第 3 表

	変形形態
比較合金 1	粒界破壊
〃 2	〃
〃 3	〃
〃 4	〃
〃 5	〃
本発明合金 6	〃
〃 7	延性変形
〃 8	〃
〃 9	〃
〃 10	〃
〃 11	〃
〃 12	粒界破壊
〃 13	〃
〃 14	延性変形
〃 15	粒界破壊
〃 16	〃
〃 17	〃
〃 18	延性変形
〃 19	〃
〃 20	〃

4. 図面の簡単な説明

第1図は耐溶接割れ性の試験に用いる厚さ1㎜の合金パイプ断面図，第2図は耐溶接割れ性試験装置の概略説明図である。

1：厚さ1㎜の合金パイプ（長さ10㎜）

2：自由落下体（重量200gw）

3：支持台

4：加熱保持炉

a：パイプ内径（φ20㎜）

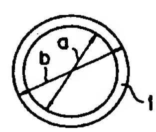
b：パイプ外径（φ22㎜）

c：落下体2の落下距離（50㎜）

特許出願人　日本鉱業株式会社

代理人　弁理士（7569）並川啓志

第1図



第2図